# HINDERED ARYL KETENES

BY

LEONARD JAMES ARMSTRONG

A.B., St. Olaf College, 1937

M.S., North Dakota Agricultural College, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1942

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## HINDERED ARYL KETENES

### Introduction

Recent studies[1, 2, 3] of vinyl alcohols make it appear that they owe their stability to the space exigency at the *beta* rather than at the *alpha* carbon atom. Vinyl alcohols are generally supposed to form as intermediates in the addition of molecules of the HA type (water, alcohols, etc.) to ketenes. The present work was undertaken because it appeared that hindered aryl ketenes might afford an independent synthesis of vinyl alcohols.

### Discussion of Results

If one of the substituents on the *beta* carbon atom of a vinyl alcohol is a mesityl or other hindering group and the other is any substituent (not hydrogen) it appears that the alcohol will be stable. Whether any restriction is to be placed on the size of the substituent on the *alpha* carbon atom is not yet apparent. Consequently ketoketenes should yield stable vinyl alcohols whereas aldoketenes would lead to alcohols which ketonize spontaneously. Experiment has confirmed this prediction.

Two aldoketenes were studied, mesitylketene and 2,4,6-triethylphenylketene. The method of preparation was that used by Staudinger[4] for phenylketene and is illustrated: mesitylglyoxal → mesitylglycolic acid → $\alpha$-bromomesitylacetyl bromide → mesitylketene. Mesitylketene was also prepared by the method of Schroeter:[5] mesitylglyoxal monohydrazone → mesityldiazomethane → mesitylketene.

Neither aldoketene could be isolated in the pure form. Each reacted with water to yield the corresponding substituted acetic acid and exhibited a pronounced tendency to dimerize. Condensation of mesitylketene with mesitylmagnesium bromide led to the formation of desoxymesitoin. Treatment of the Grignard addition product with benzoyl chloride yielded the benzoate of the enol. The instability of the enol was made evident by the observation that hydrolysis

of the benzoate yielded only desoxymesitoin.

Mesitylphenylketene and dimesitylketene were prepared from the monohydrazones of the respective diketones by the method of Schroeter.[5] Mesitylphenylketene was isolated in impure form. Reaction with water and ammonia converted it, respectively, to mesitylphenylacetic acid and mesitylphenylacetamide. Methylmagnesium iodide yielded the stable vinyl alcohol, 1-mesityl-1-phenyl-1-propen-2-ol. Hydrogenation of the ketene produced an oil which appeared to be mesitylphenylacetaldehyde. No trace of the enol form prepared by Weinstock[6] could be detected.

Dimesitylketene was not isolated. The hydration product, dimesitylacetic acid, was obtained. The principal product found in the preparation of the ketene was a white solid believed to be the lactone from dimesitylglycolic acid.

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## VITA

The author was born near Northfield, Minnesota, on March 27, 1917. He attended the elementary schools of Farmington and Northfield, Minnesota and was graduated from Polytechnic High School, Long Beach, California in June, 1933. In the following September he entered St. Olaf College in Northfield, from which he was granted an A. B. degree in June, 1937. The next two years he served as a graduate assistant in chemistry at the North Dakota Agricultural College and received the M. S. degree at the end of this period. During the past three years he has been engaged in graduate work in chemistry at the University of Illinois, where he held a teaching assistantship during the years 1939-1941 and a University Fellowship in 1941-1942.

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